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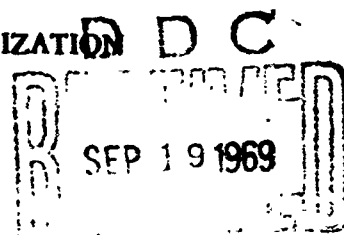
**The Aerospace Corporation Shell 405
Catalyst Evaluation Program
Volume I: Physical and Catalytic Properties**

Prepared by S. M. KING, P. C. MARX, and DAVID TAYLOR
Aerodynamics and Propulsion Research Laboratory

69 AUG 15

Laboratory Operations
THE AEROSPACE CORPORATION

Prepared for SPACE AND MISSILE SYSTEMS ORGANIZATION
AIR FORCE SYSTEMS COMMAND
LOS ANGELES AIR FORCE STATION
Los Angeles, California



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THE AEROSPACE CORPORATION SHELL 405
CATALYST EVALUATION PROGRAM
Volume I. Physical and Catalytic Properties

Prepared by
S. M. King, P. C. Marx, and David Taylor
Aerodynamics and Propulsion Research Laboratory

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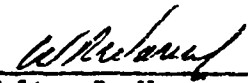
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FOREWORD


This report is published by The Aerospace Corporation, El Segundo, California, under Air Force Contract No. F04701-69-C-0066.

This report, which documents research carried out from January 1968 to June 1969, was submitted on 1 August 1969 to Lieutenant Harold D. Gibbs, SMTAE, for review and approval.

Approved


Walter R. Warren, Director
Aerodynamics and Propulsion
Research Laboratory

Publication of this report does not constitute Air Force approval of the report's findings or conclusions. It is published only for the exchange and stimulation of ideas.


Harold D. Gibbs
2nd Lt., United States Air Force
Project Officer

ABSTRACT

Results are presented for a series of physical tests performed on Shell 405 catalysts and carriers to determine the principal attrition and loss mechanisms occurring during motor operation. It is shown that the development of free space in a reaction chamber can lead to serious attrition losses. Results of vibration, mechanical crushing, thermal shock, and thermal expansion measurements are also discussed.

A laboratory technique was devised for studying catalytic activity. A thermocouple was used to measure the temperature transient occurring when a drop of hydrazine contacts catalyst. The effect of the initial pressure (vacuum to 760 torr) and temperature (-20°C to 75°C) on the reaction induced temperature change was studied and is discussed. Some correlations with motor performance data are made.

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I. INTRODUCTION

The successful operation of hydrazine monopropellant thrust systems, either in use or under development for the U. S. Air Force, is dependent on Shell 405 catalyst. A study of the development program has revealed that insufficient knowledge is available of the physical properties of the catalysts and catalyst attrition mechanisms observed during motor firings. To further complicate the problem, suppliers of propulsion systems have requested variation in catalyst processing to obtain a more durable product.

A test program on Shell 405 catalysts, and the carriers used for their preparation was initiated by The Aerospace Corporation¹ with the following objectives: (1) Study and determine catalysts attrition mechanisms, and (2) Determine the effects of carrier and catalysts processing on physical properties of catalysts and catalyst attrition. At the start of the program, the desired catalysts were not available and a study was undertaken of several available catalyst carrier samples to determine if the proposed experiments would be adequate.²

As part of a general program of evaluating hydrazine decomposition catalysts, a laboratory method of studying catalytic activity was developed. Activity testing has been a long-standing problem associated with hydrazine catalysts. Reactor ignition delay time is one measure of activity but a poor measure of intrinsic activity because of its dependence on reactor design. Several laboratory tests have been used, including liquid and vapor phase testing (Ref. 1). While these tests can be used to screen catalysts and measure decomposition rates, they fail to simulate the rapidly increasing temperature and pressure conditions of a reactor that determine the ignition characteristics. Rather than hold both temperature and pressure constant, we chose to study the temperature transient when a drop of hydrazine contacted a pellet or few granules of catalyst. A

¹J. L. Jennings, Shell 405 Catalyst: Aerospace Test Program, ATM-68(3112-32)-10 (31 May 1968).

²Results were reported to J. Russi 25 July 1968 and 10 October 1968.

thin thermocouple embedded in the catalyst was the temperature transducer. The pressure was held constant for each test, but could be varied using a bell jar test chamber. Except for the pressure effect, this test is a good approximation of the ignition phenomenon occurring in a reactor. The mechanism of the catalytic decomposition of hydrazine has been discussed in other reports (Refs. 1 and 2) and is not included here.

II. CATALYST MATERIALS

The Shell 405 catalyst is composed of two components: (1) a high-surface-area aluminum oxide carrier, and (2) the active metal, iridium. The iridium constitutes 31 to 33 weight percent of the catalyst. The exact details of the manufacturing process are proprietary information.

The catalyst is available in several particle sizes. Granular catalysts are furnished in sizes defined by U. S. Standard sieve numbers, and are available in the following ranges: 8 to 12, 14 to 18, 20 to 25, 25 to 30, and 20 to 30 mesh. The granular size catalyst is produced from carrier that has been air- or water-attrited to remove sharp edges and to partially "round" the particles.

An earlier form of the catalyst, designated ABC, was on a slightly attrited support. Granular catalyst is currently produced from support that has been air- or water-attrited to approximately 50 weight percent of original carrier weight. This catalyst is designated ABS_A if air attrited, and ABS_W if water attrited.

One user of 25 to 30 mesh catalyst has specified precalcination of the alumina support. This is carried out at 900°C for 1 hr.

The alumina carrier for the granular catalyst is supplied by Reynolds Aluminum Company (Type RA-1) with a minimum B.E.T. surface area of 160 m² per gm (Ref. 2).

Catalyst pellets are available in 1/8-in. diam. by 1/8-in. length, and are designated AAT 1/8. The alumina carrier is supplied by Harshaw Chemical Company (Type 1404) with a minimum B.E.T. surface area of 160 m² per gm (Ref. 2).

Most of the catalyst attrition studies were performed using 25 to 30 mesh carrier and catalyst.

III. CATALYST ATTRITION MECHANISMS

A. MECHANICAL ATTRITION

The degree to which mechanical attrition, the physical movement of the catalyst particles against each other, causes loss of catalyst from a reaction chamber is a matter of concern. The Shell 405 catalyst, with its large surface area, shows relatively poor resistance to mechanical abrasion, since fines can be produced by vigorous hand shaking of a sample in a glass vial. Even though the catalyst beds are initially loaded with no void space, free space may result from shrinkage of the catalyst or other sources; thus, the effects of gas blasts due to motor pulsing and normal vibration of the catalyst motors presented potential attrition sources.

Prior to carrying out the mechanical attrition tests and the crushing tests, the loading and screening techniques were examined to determine if noticeable attrition resulted. All chambers were vibration-packed using a 52.5-gm piston (load of 0.59 lb per in.²) to settle the material to a constant depth. The procedure did not produce significant attrition of the carriers or catalysts.

The reported data were obtained by using a fixed bed depth of catalyst and subsequently screening into various sieve size fractions. The weights were then converted into average weight percents retained by or passing through No. 30, 30 to 40, 40 to 60, and 60 mesh screen. Three samples were normally run; however, when tests indicated that 95 weight percent or more of the sample was retained on the No. 30 mesh screen only two samples were run to conserve time and effort.

The carriers and catalysts (U.S. Sieve size 25 to 30) examined during this phase of the program are given in Table 1, together with the average weight percent sieve size of two samples screened to determine if a significant difference in size distribution existed.

Figures 1 through 3 are photographs of the carrier and catalysts (U.S. Sieve size 25 to 30), including a sample of RA-1 untreated carrier. A comparison of Fig. 1 with Figs. 2 and 3 shows the effects of air- or water-attriting to approximately 50 percent of the original weight.

Table 1. Initial Size Distribution Determination

Carrier	Average wt %, U.S. Sieve Size			
	> 30	30-40	40-60	< 60
ABSG, air-attrited	98.0	2.0	< 0.1	< 0.1
ABSG, air-attrited (calcined 900°C for 1 hr)	96.8	3.2	< 0.1	< 0.1
ABSG, water-attrited	99.4	0.6	< 0.1	< 0.1
<u>Catalyst</u>				
ABSG, air-attrited	99.3	0.7	< 0.1	< 0.1
ABSG, air-attrited (calcined carrier)	99.3	0.7	< 0.1	< 0.1



Figure 1. KA-1 As-Received Carrier



Figure 2. ABSG Water-Attrited Carrier



Figure 3. ABSG Air-Attrited Carrier

1. GAS BLAST STUDIES

A Lucite chamber was fabricated to provide a 0.50-in.-diam. by 1.6 in.-length chamber. The dimensions corresponded with the metal reaction chamber used at the The Aerospace Corporation to study the injection-ignition process of the catalytic decomposition of hydrazine. A 0.40-in. bed length at the end normally used for gas injection was obtained by using a 1.2-in. spacer with a 60-mesh screen on one end to retain the catalyst. Three bed densities of 0, 5, and 10 percent, excluding intergranular voids, were obtained by vibration-packing the catalyst using the 52.5-gm position piston. The 5 and 10 percent void volumes were determined by depth-gauging the chamber. It was anticipated that the 5 and 10 percent void volumes would show a corresponding weight change, however they were not as consistent as desired. The bed densities of 0, 5, and 10 percent void volumes were examined for gas-blast attrition by subjecting the bed to 1720 gas pulses (0.5 sec On, 1 sec Off) at chamber pressure of approximately 125 psi. The gas blast was directed in an upward direction to permit maximum carrier movement during testing. The carrier was then screened and the results are reported in Table 2.

The results for the ABSG air-attrited carrier indicated some attrition for the 10 percent void space tests, but no detectable loss of the carrier from the chamber was observed. The ABSG air-attrited and calcined carrier apparently was attrited to a slight extent for the 0 and 5 percent void space loading, and showed greater attrition for the 10 percent space loading. However, no detectable loss from the chamber was observed when initial and final carrier weights were compared. On the basis of Table 2 data, the ABSG water-attrited carrier appears to be the best carrier.

No appreciable attrition was indicated for the 0 and 5 percent void space loadings during testing of two catalysts. Significant attrition and some loss of the catalyst from the test chamber was observed for the 10 percent void space tests.

2. VIBRATION TESTS

The Lucite chamber was vibration-packed using the same bed depth (0.40 in.) and packing technique as for the gas blast tests. The Lucite chamber was positioned on an electromagnetic vibration exciter so that the direction of generated

Table 2. Gas Blast Attrition in Upward Direction^a

Carrier	Weight, gm	Average wt%, U.S. Sieve Size			
		> 30	30-40	40-60	< 60
ABSG, Air-Attrited					
Fully packed	1.46	97.7	2.3	< 0.1	< 0.1 ^b
5% void space	1.41	97.6	2.4	< 0.1	< 0.1 ^b
10% void space	1.35	95.1	4.9	< 0.1	< 0.1 ^b
ABSG, Water-Attrited					
Fully packed	1.47	97.9	2.1	< 0.1	< 0.1 ^b
5% void space	1.43	99.3	0.7	< 0.1	< 0.1 ^b
10% void space	1.36	99.3	0.7	< 0.1	< 0.1 ^b
ABSG, Air-Attrited (Calcined 900°C, 1 hr)					
Fully packed	1.36	95.9	4.1	< 0.1	< 0.1 ^b
5% void space	1.32	95.8	4.2	< 0.1	< 0.1
10% void space	1.25	91.8	7.3	0.8	< 0.1
<u>Catalyst</u>					
ABSG, Air-Attrited Carrier					
Fully packed	2.09	98.6	1.4	< 0.1	< 0.1
5% void space	1.98	98.3	1.8	< 0.1	< 0.1 ^b
10% void space	1.88	84.1	7.8	2.7	0.7 (4.7% lost)
ABSG, Air-Attrited Carrier (Calcined 900°, 1 hr)					
Fully packed	2.05	98.3	1.7	< 0.1	< 0.1
5% void space	1.95	97.9	1.5	0.5	< 0.1
10% void space	1.85	92.8	3.8	0.9	< 0.1 (2.5% lost)

^a0.40-in. bed depth, 1700 pulses @ 125 psi.^bTwo samples obtained.

forces were at right angles to the length of the catalyst bed. The samples were exposed to vibration for 10 min at a level equivalent to 1.0 g^2 per cps between 400 and 100 Hz using 11 cycle increments of 55 sec duration each. The samples were then screened and classified; the results are given in Table 3. The vibration tests as conducted do not appear to be a source of severe attrition.

B. MECHANICAL CRUSHING STUDIES

Mechanical crushing studies were initiated to determine if the various processes used on carriers and catalysts improved their physical strength and resistance to fragmentation. Single-stroke compression and repeated cycle loading tests were conducted on a number of carriers and catalysts.

1. SINGLE-STROKE CRUSHING TESTS

Samples of 25 to 30 mesh carriers and catalysts were loaded to a depth of 0.23 in. in a 0.50-in. die. A 52.5-gm piston provided a load of 0.59 lb per in.² as the carrier was vibration-packed to settle the material. Screening of the material after packing to a constant depth did not reveal any significant attrition of the carrier from the loading process. Crushing strength determinations were then made by compressing the samples 0.02 in. and 0.04 in. and classifying them in U.S. Sieve sizes retained by No. 30, 30 to 40, 40 to 60, or passing through No. 60 mesh screen. Tests were conducted on three samples of each carrier and catalyst; the results are given in Table 4.

Since it was noted that the carriers rapidly adsorbed moisture, samples were left exposed to ambient conditions until a constant weight was reached, and then compressed 0.02 in. Test results for the air-attrited carrier that contained 13.3 percent adsorbed moisture were more favorable than those for the unexposed carrier. Tests results for the water-attrited carrier that contained 14.4 percent adsorbed moisture were similar to those obtained for the unexposed material.

The ABSG air-attrited and calcined carrier displayed a marked decrease in load bearing capability compared with the uncalcined, air- and water-attrited carriers. Overall, the water-attrited carrier displayed more favorable

Table 3. Vibration Test Results^a

Carrier	Weight, gm	Average wt %, U.S. Sieve Size			
		> 30	30-40	40-60	< 60
ABSG, Air-Attrited					
Fully packed	1.38	97.0	3.0	< 0.1	< 0.1
5% void space	1.33	97.3	2.7	< 0.1	< 0.1
10% void space	1.35	97.9	2.1	< 0.1	< 0.1
ABSG, Water-Attrited					
Fully packed	1.38	98.8	1.2	< 0.1	< 0.1
5% void space	1.34	99.1	0.9	< 0.1	< 0.1
10% void space	1.26	99.0	1.0	< 0.1	< 0.1
<u>Catalyst</u>					
ABSG, Air-Attrited Carrier					
Fully packed	2.09	99.1	0.9	< 0.1	< 0.1 ^b
5% void space	1.98	99.3	0.7	< 0.1	< 0.1 ^b
10% void space	1.88	98.7	1.3	< 0.1	< 0.1 ^b

^a0.40-in. bed depth, 400-1000 cps @ 1.0g²/cps.

^bTwo samples obtained.

Table 4. Single Stroke Crush Test Results^a

Carrier	0.02-in. Compression						0.04-in. Compression					
	Weight, gm	Pressure, lb/in. ²	Avg. wt %, U.S. Sieve Size			Avg. Pressure, lb/in. ²	Avg. wt %, U.S. Sieve Size					
			> 30	30-40	40-60 < 60		> 30	30-40	40-60 < 60			
ABSG, air-attrited	0.87	1722	78.7	11.1	4.6	5.7	4213	57.2	16.3	10.0	16.6	
ABSG, air-attrited (13.3% moisture adsorbed)	0.94	1752	85.0	7.8	3.2	4.0						
ABSG, air-attrited (14.7% moisture adsorbed)	0.95	1798	85.4	6.6	3.3	4.7	4065	60.9	14.5	8.7	16.0	
ABSG, air-attrited (vac. dried 100°C, 18 hr)	0.84	2150	85.6	7.4	3.2	3.9						
ABSG, air-attrited (calcined 1000°C, 3 hr)	0.78	1248	87.1	6.7	2.5	3.8						
ABSG, air-attrited (calcined 900°C, 1 hr)	0.78	1432	86.0	7.6	2.5	3.8	3444	65.6	13.8	7.3	13.3	
ABSG, water-attrited	0.86	2165	88.9	4.5	3.0	3.7	5115	62.3	13.3	8.9	15.5	
ABSG, water-attrited	0.92	2196	85.5	6.6	3.6	4.4	4371	60.8	14.1	9.2	15.9	
ABSG, water-attrited (14.4% moisture adsorbed)	0.94	1857	87.0	5.4	3.3	4.3						
RA-1 untreated carrier	0.70	417	84.8	10.2	2.3	2.7	942	65.6	17.3	7.5	9.5	
<u>Catalyst</u>												
ABSG, air-attrited carrier	1.20	1768	85.3	6.4	3.3	5.0	4036	64.5	13.2	7.4	14.4	
ABSG, air-attrited carrier (calcined 900°C, 1 hr)	1.18	1758	87.2	6.0	3.2	3.7	4045	61.6	13.7	8.6	16.1	

^a0.23-in. depth, 0.5-in.-diam mold.

load-bearing characteristics than the air-attrited carrier during single-stroke compression. The attrited carriers displayed much greater load-bearing capabilities than the KA-1 untreated carrier.

Test data did not indicate the superiority of either the water- or air-attrited carriers.

The ABSG catalysts produced from air-attrited and air-attrited-calcined (900°C for 1 hr) carriers were examined and displayed very similar load-bearing and fragmentation characteristics (Table 4).

As anticipated, both carriers and catalysts indicated some correlation between fragmentation and degree of compression.

2. REPEATED LOADING TESTS

A sample of the carrier was loaded into the 0.50-in. die as described above for the crush tests. The sample (0.23-in. depth) was then compressed 0.02 in., and the load required to obtain the 0.02-in. compression was observed. The load was then set on the Kiehle tester and three samples were cycled to the same load 5, 20, and 100 times. The final deflection was observed, and the samples screened to determine the average weight fractions; the results are given in Table 5.

The fragmentation of both carrier and catalyst granules increased as cycling was increased. Both carriers and catalyst showed a correlation between fragmentation and final degree of compression, whether single-stroke or repeated-loading. The load-bearing capability of the air-attrited carrier averaged approximately 10 percent below that of the water-attrited carrier; that of the air-attrited-calcined carrier averaged approximately 45 percent below that of the water-attrited carrier. On the basis of test data the water-attrited carrier appears to have superior load-bearing capability, but does not show any marked superiority in fragmentation characteristics.

C. THERMAL SHOCK RESISTANCE

Resistance to thermal shock is a measure of the ability of a material to resist weakening or fracture when subjected to sudden heating and cooling.

Table 5. Repeat Loading Crush Test Results^a

Carrier	Weight, gm	Avg. Initial Pressure, lb/in. ²	Final Deflection, in.	Avg. wt %, U.S. Sieve Size			
				> 30	30-40	40-60	< 60
ABSG, Air-Attrited							
5 cycles	0.84	2083	0.024	76.7	11.4	5.4	5.5
20 cycles	0.84	2175	0.030	69.9	13.5	6.8	9.8
100 cycles	0.84	2094	0.038	59.6	15.4	9.0	16.1
ABSG, Water-Attrited							
5 cycles	0.85	2302	0.024	82.7	6.6	4.6	6.1
20 cycles	0.85	2282	0.033	72.9	10.3	6.5	10.3
100 cycles	0.85	2450	0.037	61.7	13.1	8.6	16.5
ABSG, Air-Attrited (calcined 900°C, 1 hr)							
5 cycles	0.79	1355	0.024	81.5	9.9	3.5	5.1
20 cycles	0.79	1250	0.027	77.5	11.2	3.9	7.4 ^b
100 cycles	0.79	1219	0.036	64.8	15.4	7.1	12.8 ^b
Catalyst							
ABSG, Air-Attrited Carrier							
5 cycles	1.20	1808	0.024	79.1	9.1	4.4	7.4
20 cycles	1.20	1783	0.031	67.6	12.1	6.4	13.9
100 cycles	1.20	1768	0.037	63.9	13.0	7.7	15.5
ABSG, Air-Attrited Carriers (calcined 900°, 1 hr)							
5 cycles	1.18	1763	0.023	81.2	8.5	4.3	6.0
20 cycles	1.18	1661	0.027	74.4	10.8	5.7	9.1
100 cycles	1.18	1701	0.035	64.7	13.2	7.8	14.4

^a0.23-in. depth; 0.50-in. mold; 0.02-in. initial deflection

^bTwo samples.

There are no standard tests that will accurately evaluate this property. In our test procedure, the catalyst was heated in an open quartz tube to 1000°C and quenched with a jet of water which dropped the temperature from 1000°C to 100°C in approximately 0.5 sec. Excellent thermal shock resistance was indicated by both the catalyst pellets and granules. Six heat and quench cycles were run with a sample of ten pellets and ten 14 to 18 mesh granules, with no evidence of fracture.

D. THERMAL EXPANSION AND CRUSHING

Thermal expansion of the catalyst bed could lead to particle crushing and severe losses. The limits of bed expansion and contraction were determined from coefficient of expansion measurements made on granular and pellet Shell 405 catalyst using a Leitz dilatometer, Model UDB, with a temperature limit of 1080°C; the data are summarized in Table 6. Each run represents a single 6-hr heating and cooling cycle from 25°C to 1080°C, and back to 25°C. In Run A, using a single 1/8-in. pellet, a net shrinkage of 1.2 percent was recorded at 1000°C. At the completion of the cycle, the net shrinkage had increased to 4.8 percent. Run B represents the first of a series of three cycles run with a packed quartz tube of 25 to 30 mesh ABS_AG catalyst. Two quartz rod plungers at each end of the tube provided contact with the train of granules and allowed sensing of their relative contraction or expansion. Up to 1000°C, the granule train tended to expand, with the net expansion increasing with each cycle. In Run D, this expansion approximated the linear expansion of fully dehydrated alpha alumina, which expands 0.9 percent from 25°C to 1000°C. The full cycle resulted in a net shrinkage, however, and shrinkage continued after completion of three cycles. This can be correlated with the conversion of hydrated alumina to the alpha form, a process which is accompanied by shrinkage and is slow even at 1080°C.

The results of the thermal expansion and crushing tests indicate that a bed of granular catalyst will continue to shrink after several extended heating cycles. The net expansion at 1000°C, however, continues to increase with each cycle. Reactor attrition losses, if they occur, will be determined by bed depth, packing mode, temperature gradient, and reactor duty cycle.

Table 6. Thermal Expansion Data

Run	Specimen	Initial Length, mm	Net Change ^a at 1000°C, mm	Net Change ^{a,b} After One Cycle, mm	Shrinkage After One Cycle, percent ^b
A	AAT 1/8	3.33	-0.040	-0.16	4.81
B	ABS _A G 25-30 mesh, 1st cycle	15.0	+0.015	-0.075	0.50
C	ABS _A G 25-30 mesh, 2nd cycle	14.9	+0.050	-0.110	0.74
D	ABS _A G 25-30 mesh, 3rd cycle	14.8	+0.085	-0.06	0.41

^a+ expansion; - contraction.

^bcycle: 25°C → 1080°C → 25°C.

IV. CATALYST ACTIVITY STUDIES

A. TEST PROCEDURE

Catalyst activity was studied by measuring the rate and magnitude of the temperature rise occurring when a measured drop of hydrazine was allowed to contact a catalyst pellet or granule. The temperature transducer was a chromel-alumel thermocouple embedded in the catalyst surface. The initial catalyst temperature was varied from -20°C to $+75^{\circ}\text{C}$ by directing a stream of dry, refrigerated or heated nitrogen over the surface until the desired temperature was reached. A hypodermic needle was used to apply a drop of hydrazine to the catalyst, with the resulting temperature transient (Fig. 4) plotted by an X-Y recorder. The initial pressure was varied from vacuum to 760 torr using a special bell jar reactor. With this reactor it was also possible to observe the effect of various gases, such as nitrogen, ammonia, and oxygen, on the temperature transient.

B. EXPERIMENT RESULTS AND DISCUSSION

The pressure dependence of the temperature transient is shown in Fig. 5. The magnitude of the initial temperature change ΔT is plotted against the ambient bell jar pressure. Vacuum ignitions ($< 30\mu$) resulted in evaporative cooling down to the freezing temperature of hydrazine, and in some cases as low as -9°C (supercooling). Thus, the exothermic decomposition reaction was delayed for up to 10 sec while the catalyst thawed out. This cooling effect allowed a deeper than normal penetration of liquid hydrazine into the porous catalyst, and resulted in severe spalling of the 1/8-in. pellets because the gases generated by the reaction were released too slowly. Catalyst granules did not display spalling during ignitions, and this is correlated with their more open-pore structure (Fig. 6). The evaporative cooling effect diminished as the pressure increased until, at 16 torr, no temperature change could be recorded within the first 500 ms of injection. At higher pressures, the magnitude of the initial temperature rise increased, reaching 70°C at 760 torr.

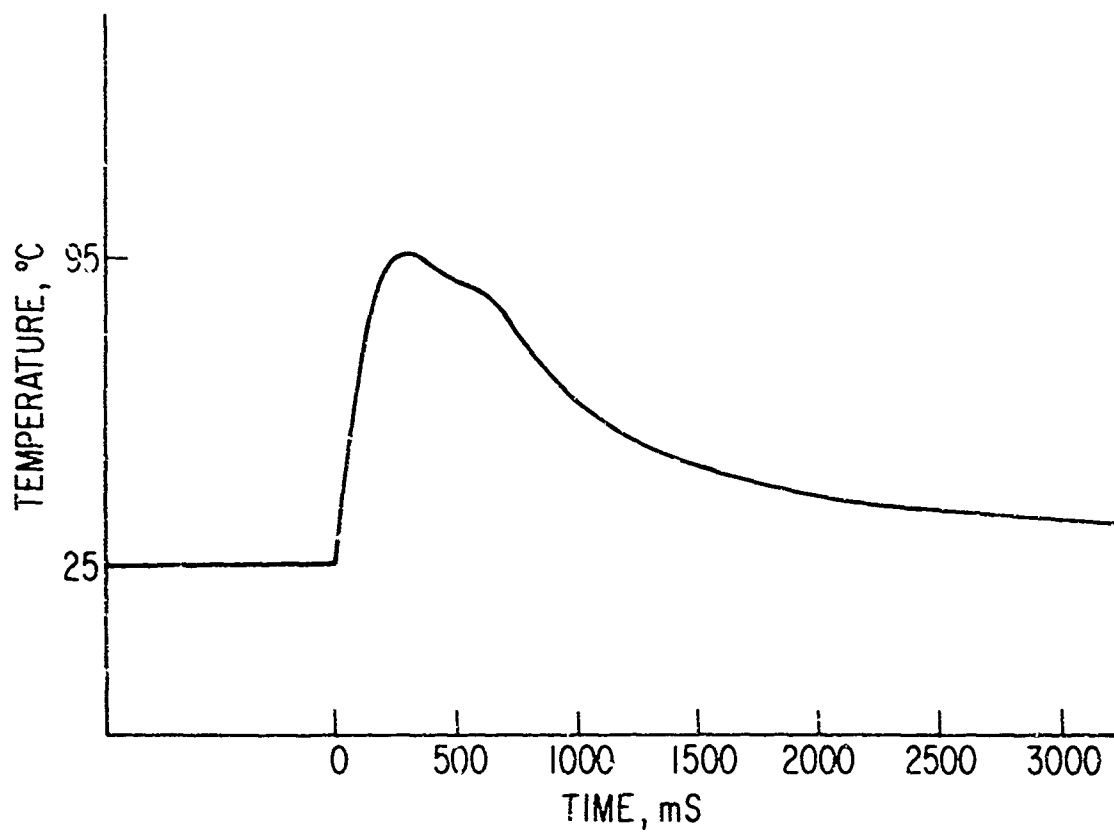


Figure 4. Hydrazine-Catalyst Temperature Transient at 25°C and 760 torr

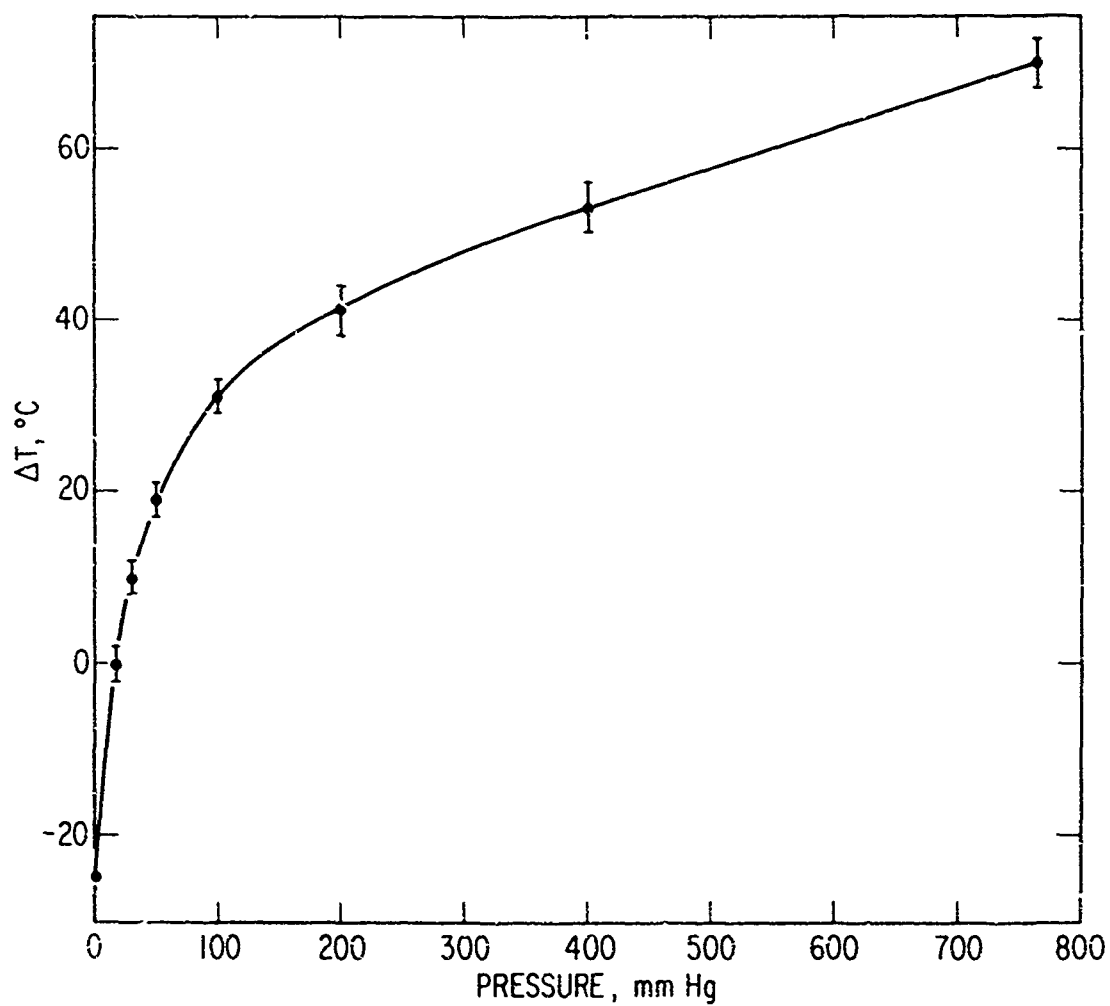


Figure 5. Initial Temperature Rise vs Ambient Pressure at 25°C

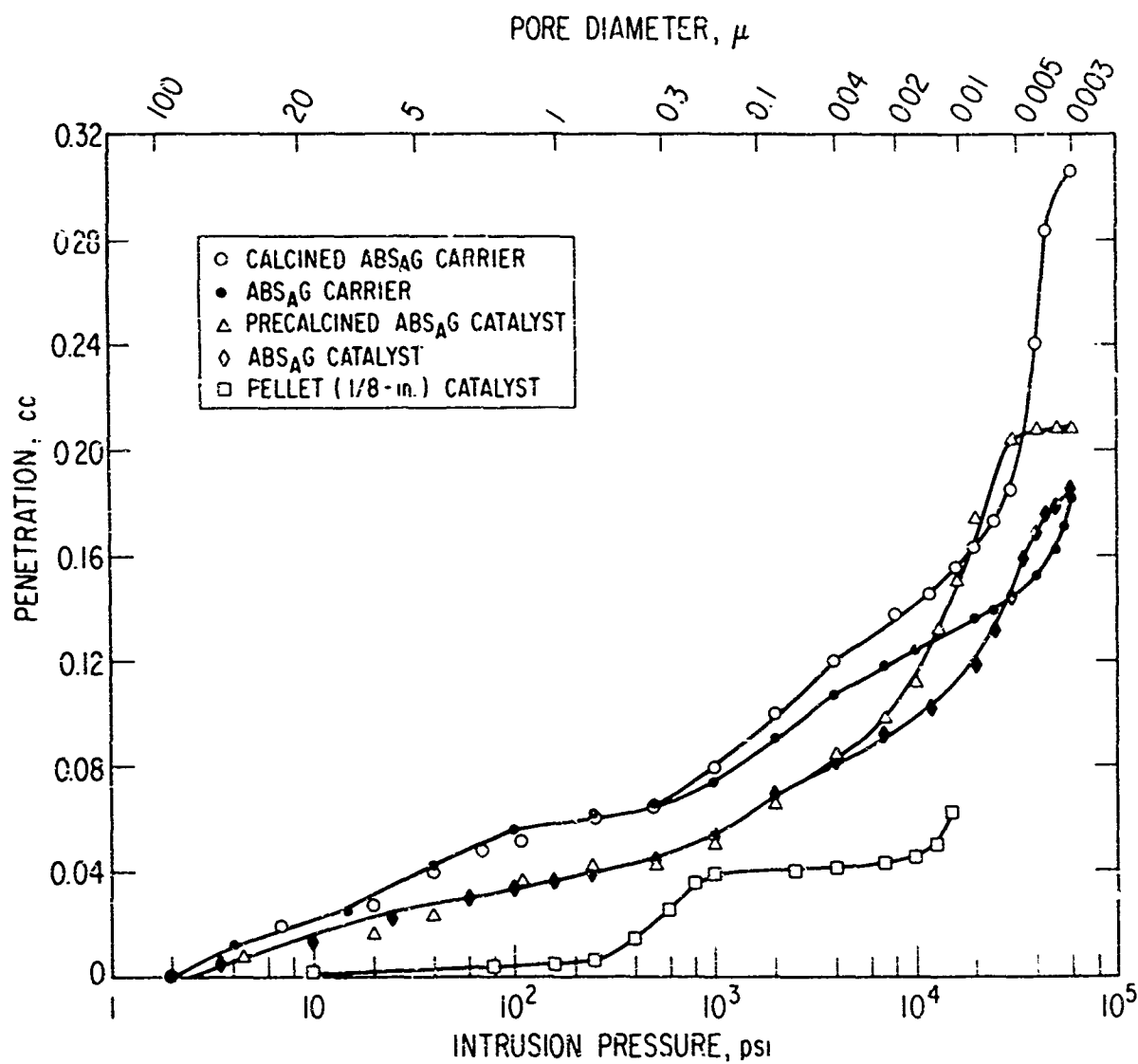


Figure 6. Mercury Intrusion Porosity Determination

No significant difference was observed in the temperature rise for 1/8-in. pellets, 25 to 30 mesh, 14 to 18 mesh, and 8 to 12 mesh granules in this pressure range. The volume of the bell jar reactor (400 cc) was large enough so that the pressure fluctuation during the injection of hydrazine did not exceed 1 torr. In the above runs the temperature increased at a rate of 420°C per sec, which is the limiting response of the thermocouple-recorder system.

The saturation loading of hydrazine per charge of catalyst was determined for each mesh size (Fig. 7); larger ratios caused performance deterioration due to the thermal drag of excess liquid hydrazine. The hydrazine-to-catalyst ratio for the granules exceeded their pore volume, while that for the 1/8-in. pellet was slightly lower than the pore volume. The shape of Fig. 7 can be correlated with the surface-to-volume ratio variation with mesh size.

The measured temperature rise is determined by a balance between the exothermic catalytic reaction and the endothermic evaporation of liquid hydrazine. The heat released catalytically is proportional to the rate and depth of liquid penetration into the porous catalyst, which is controlled by the positive ambient and capillary pressures and the negative back pressure due to accumulating decomposition gases. Since the capillary and back pressures are fixed by the pore structure, the ambient pressure determines the penetration depth, heat release, and temperature rise. At a pressure of 16 torr, the catalytic heat release just balanced the evaporative heat loss; at higher pressures, the exothermic reaction was dominant. Because no plateau was reached at 760 torr, the initial temperature rise should continue to increase with increasing pressures above atmospheric. This is an important consideration in reactor motor firings where the confined volume leads to a rapid pressure buildup.

The rate and magnitude of the temperature rise associated with liquid hydrazine at 25°C are much greater than for gaseous hydrazine. This is because the liquid penetration rate, from the action of the ambient and capillary forces, is much faster than the rate of gaseous diffusion. However, once the first monolayer of liquid has reacted, an excess of liquid can retard,

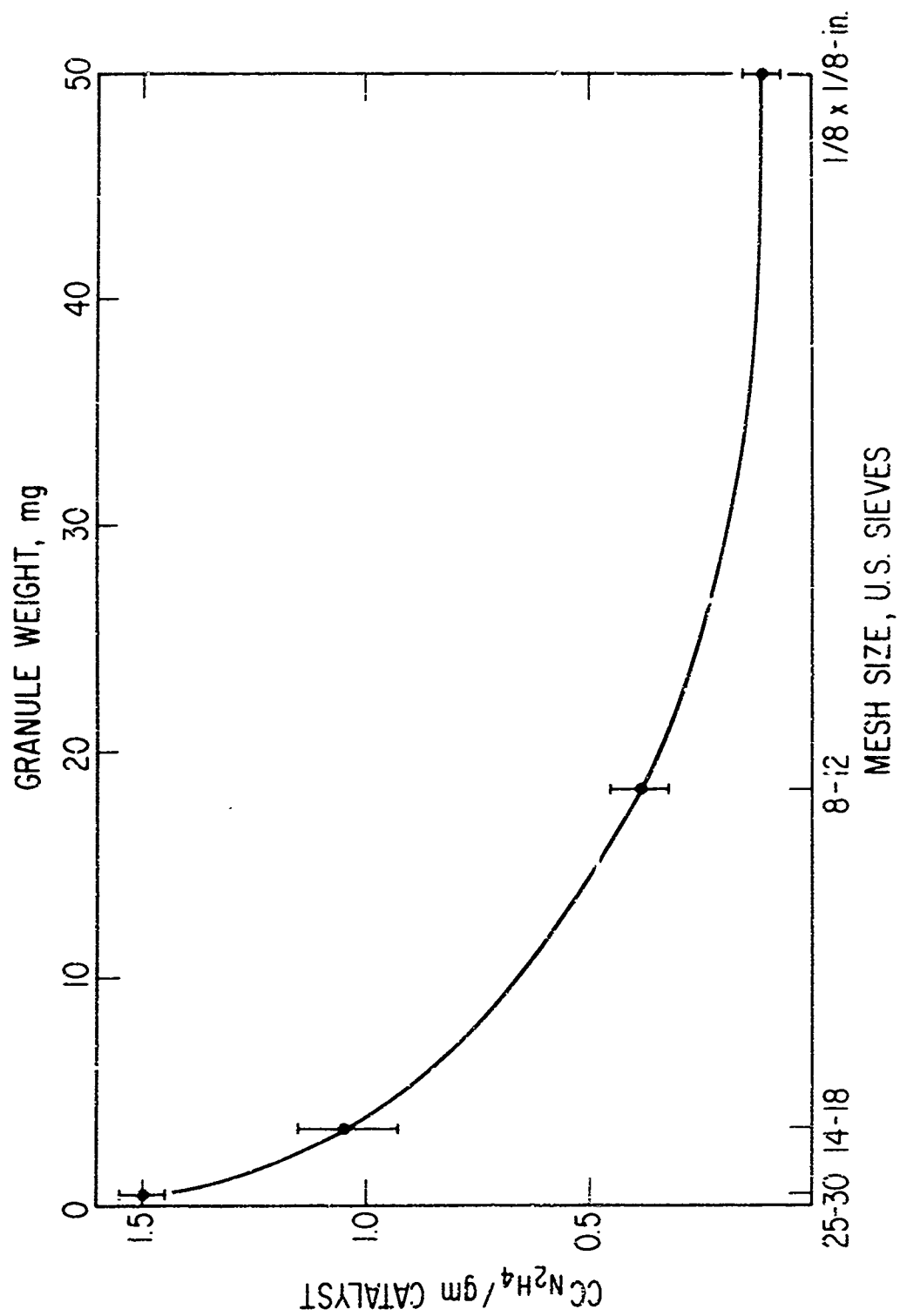


Figure 7. Saturation Loading Ratio of Hydrazine to 405 Catalyst at 25°C

and even quench, the reactions due to its high heat capacity. Liquid is needed for a fast ignition, but the liquid-to-catalyst ratio must be optimized to ensure the most rapid rate of temperature and pressure rise into the regime of film boiling.

The temperature rise at a given pressure was found to be independent of the ambient gas. The same initial increase was observed with oxygen as with nitrogen. However, a large secondary peak was observed as oxygen diffused into the pores to react with excess liquid hydrazine. It is apparent that the state of the catalyst in terms of intrinsic activity, surface area, and cleanliness of the iridium determines the temperature rise at a given pressure.

At 25°C, in air, the as-received catalyst has approximately 0.3 atoms of chemisorbed oxygen per atom of iridium (Ref. 3). The first ignition, therefore, will involve the oxidation of hydrazine in addition to the decomposition reaction. This oxygen layer is removed for subsequent vacuum firings reducing the net heat release. A test apparatus was designed to measure the temperature rise of hydrazine on reduced iridium. The catalyst was reduced in hydrogen at 400°C and allowed to cool to 25°C under hydrogen before the hydrazine was applied. A temperature rise of $27 \pm 2^\circ\text{C}$ was observed, compared with the 70°C rise characteristic of the as-received catalyst.

A temperature rise of approximately 3°C was shown for hydrazine applied to a granule or pellet of alumina, the catalyst carrier. This rise is due to the heat of wetting of hydrazine on alumina. The contribution is small compared with the catalytic reaction.

The rate and magnitude of the temperature rise also were studied as a function of the initial catalyst temperature (Table 7). Above 25°C, the rise was limited by a peak temperature of $95 \pm 5^\circ\text{C}$; at lower temperatures, the magnitude and rate of the temperature rise decreased. An Arrhenius activation energy was calculated from the temperature dependence of the rate of rise. The value, 3 kcal per mole, is actually a pseudo activation energy, since 25°C hydrazine was applied to cooler catalyst. This experiment simulates motor firings where hydrazine at storage temperature is injected into a precooled reactor. The temperature dependence of low-temperature ignition

Table 7. Magnitude and Rate of Initial Temperature Rise

Initial Temp., °C	Final Temp., °C	ΔT , °C	Rate of Rise, °C per sec
-20	20	40 ± 5	220 ± 30
0	57	57 ± 4	280 ± 30
25	95	70 ± 3	420 ± 40
40	95	55 ± 4	420 ± 40
50	95	45 ± 5	420 ± 40
60	95	35 ± 5	420 ± 40
75	95	20 ± 5	420 ± 40

delay data (Ref. 4) indicates an activation energy comparable to our value of 3 kcal per mole.

In another study it was determined that hydrazine can contain up to 30 weight percent water, 10 weight percent ammonia, or 10 weight percent carbon dioxide without affecting its temperature transient.

Outside of adsorbed oxygen, the surface area of the iridium largely determines catalyst activity. The factors that determine this surface area are: the area of the alumina substrate, metal loading, and the thermal history of the catalyst during processing and use. Each of these factors is demonstrated in Table 8. First, precalcining of the ABSG carrier at 900°C decreases the alumina surface area approximately 50 percent relative to uncalcined carrier.³ This area is measured by nitrogen gas adsorption at low temperatures. When 31 to 33 weight percent iridium is deposited on this calcined carrier, the resulting metal area, as measured by hydrogen chemisorption, is less than 50 percent of the typical catalyst value.³ The hydrogen adsorption corresponds to approximately one H atom per exposed metal atom; thus, a hydrogen chemisorption of 350 μ moles per gm of catalyst means a metal surface area of about 35 m² per gm.

The area of a given volume of alumina is changed very little by the addition of iridium to form the catalyst (Ref. 5). On a weight basis, however, the addition of iridium reduces the total area, measured by nitrogen adsorption, by the weight percentage of iridium making up the catalyst. Thus, catalyst made from 160 m² per gm alumina will have a total surface area approximately 110 m² per gm.

The catalyst total and metal surface area was greatly decreased after thermal conditioning at 1800°F. A greater loss occurred in a neutral (argon) atmosphere than in a reducing (hydrogen) atmosphere (Ref. 6). The surface diffusion and sintering of iridium, promoted by the presence of initially chemisorbed oxygen, apparently occurs more readily in a neutral atmosphere (Refs. 3 and 7). Electron micrographs of the surface of Shell 405 pellets heated in hydrogen and argon for 1 hr at 1000°C indicate more metal sintering in the argon atmosphere. Metal crystallites appeared to diffuse and concentrate

³P. Williams, Shell Development Co., Private Communication.

Table 8. Surface Area Data

Catalyst	Total Area, m^2/gm	Hydrogen Sorption, ^a $\mu\text{ moles/gm}$
Typical 405	110-130	340-400
ABSG (precalcined carrier, 900°C)	55-70	110-160
Annealed ABG (H_2 , 1 hr, 1800°F)	~ 60	~180 (estimated)
Annealed ABG (Ar, 1 hr, 1800°F)	~ 47	< 100 (estimated)
Motor-Fired ABG (1 hr ss, 1800°F)	~75-80	~200 (estimated)
AAT 1/8 (24.6 wt % Ir)	110-130	~320
AAT 1/8 (8.7 wt % Ir)	110-130	~ 200
ABSG (22 wt % Ir)	110-130	~ 300
ABSG (18.7 wt % Ir)	110-130	~280

^a Approximately ten times metal surface area in m^2/gm .

in ridges during the heat treatment; also, larger alumina crystallites were formed through partial recrystallization of the substrate.⁴

Motor-fired catalyst (reducing atmosphere) seems to suffer a lower loss of surface area than hydrogen-annealed catalyst (Ref. 6). This is probably because the entire bed did not reach the peak operating temperature of 1800°F during steady-state firing conditions.

The active metal surface area does not increase linearly with increasing catalyst metal content (Ref. 8). Several pellet and granule samples with reduced metal loadings were supplied by Shell Development Company for activity testing. The two pellet and granule catalysts included in Table 2 had activity, as measured by the thermocouple test, identical to the standard 405 catalyst. However, only the pellet sample (8.7 weight percent iridium) indicated a decrease in activity (70 percent) after annealing in hydrogen for 1 hr at 1800°F.

Hydrogen annealing, under our test conditions, probably reduces the active metal area of the 405 catalyst by at least 50 percent. The pellet sample, with 8.7 weight percent iridium, therefore, is estimated to have a hydrogen sorption value of about 100 after hydrogen annealing. ABSG prepared with precalcined carrier retains the same thermocouple activity as standard 405, although the hydrogen sorption ranges from 110 to 160. This data indicates that catalyst with hydrogen sorption values greater than 100 remain undifferentiated by the thermocouple test. The motor ignition delay time is sensitive to hydrogen sorption values lower than approximately 200, i.e., there is a significant increase in the ignition delay time over standard 405 catalyst. The thermocouple test at atmospheric pressure, therefore, is not as sensitive as an actual motor test. Higher ambient test pressures could extend the sensitivity of the thermocouple test to larger metal surface areas.

⁴R. F. Schneidmiller, "Electron Microscope Examination of Shell 405 Catalyst Heated in Argon and in Hydrogen," IOC, The Aerospace Corporation, El Segundo, California, (27 September 1968).

V. PORE SIZE DISTRIBUTION MEASUREMENTS

An Aminco 5-7125 porosimeter was used to make mercury intrusion porosity determinations of three Shell 405 catalysts and two carriers. A plot of the data, normalized to 1 gm, is given in Fig. 6. Calcining (900°C, 1 hr) standard 25 to 30 mesh ABS_AG carrier opened the smaller pores ($< 0.3\mu$) relative to uncalcined carrier thus increasing the pore volume approximately 70 percent. However, the surface area was reduced about 50 percent in the process (Table 8). The smaller pores were opened through the loss of interstitial and combined water. The corresponding catalysts (ABS_AG and precalcined ABS_AG) displayed decreased porosity due to the iridium loading of the carrier. Again, the two catalysts showed a distinct difference in pore size below 0.05μ . The pore distribution curve for the 1/8-in. pellet catalyst, while extending only to 15,000 psi, indicated a tighter-packed, less-open structure than the granular catalyst. The carrier was also different (Harshaw 1404 compared to Reynolds RA-1), and the manufacturing process involved pelletizing rather than simple air drying of the alumina gel.

VI. CONCLUSIONS

Results of the gas blast tests indicate that development of free space in a catalyst reaction chamber is a potential attrition source. In order to avoid gas blast attrition it appears advantageous to develop methods to eliminate void space due to catalyst shrinkage, slow attrition, or other potential sources.

The vibration tests, as conducted, do not indicate attrition of carriers or catalysts. It is possible that gas blast attrition may be enhanced by vibration during pulsing; however, this problem was not studied. The mechanical crushing of carriers and catalysts does not provide a satisfactory method for comparing the materials.

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<p>Results are presented for series of physical tests performed on Shell 405 catalysts and carriers to determine the principal attrition and loss mechanisms occurring during motor operation. It is shown that the development of free space in a reaction chamber can lead to serious attrition losses. Results of vibration, mechanical crushing, thermal shock, and thermal expansion measurements are also discussed.</p> <p>A laboratory technique was devised for studying catalytic activity. A thermocouple was used to measure the temperature transient occurring when a drop of hydrazine contacts catalyst. The effect of the initial pressure (vacuum to 760 torr) and temperature (20° to 75°C) on the reaction induced temperature change was studied and is discussed. Some correlations with motor performance data are made.</p>		

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